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(54) Production of hydrogen.

(57) A reactor system is provided for the delivery of hydrogen on site for hydrogen users requiring of the order of 28 to 2800 m³ hydrogen per day. The system consists of a flow through reactor in which cracked ammonia is passed over a hydride bed.
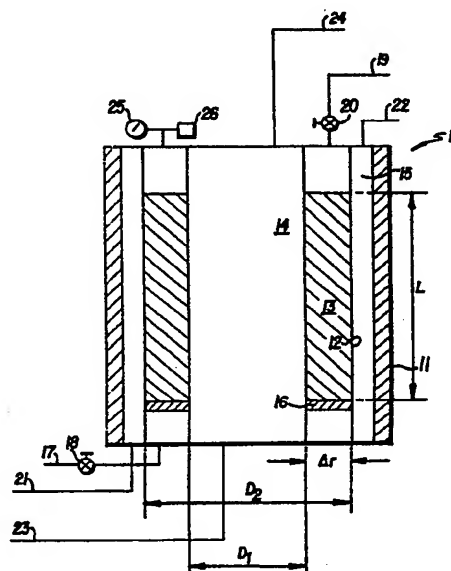
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Production of Hydrogen

The present invention relates to apparatus and a method for the production and delivery of hydrogen, and particularly to an on-site production system for hydrogen users requiring of the order of 28 to 2800 m³ of hydrogen per day.

Large industrial users of hydrogen who consume more than about 10^4 m³/day of hydrogen usually generate their own hydrogen by the steam reforming of methane. Users of less than this amount normally purchase hydrogen from a merchant supplier. Such purchasers fall into three categories, the small user, consuming around two cylinders a year, i.e. approximately 28 m³/day, the intermediate user in the range 28 m³/day to 2.8 x 10³ m³/day and the large purchaser/user consuming more than about 2.8 x 10³ m³/day. Small users have a very high unit cost since they are paying primarily for packaging and delivery. However since the quantities purchased are so small the overall annual cost is too low to justify the use of alternative sources of supply. At the other end of the scale, purchasers of more than about 2.8 x 10³ m³/day can economically buy liquid hydrogen which can be transported in large quantities at relatively low cost compared with gas transportation and such users are consequently well served. However the intermediate user of hydrogen is poorly served and pays a high unit rate. Such users are seeking more economic methods of obtaining hydrogen.

It has been proposed in US patent 4 036 944 to recover hydrogen from a waste gas stream containing a mixture of hydrocarbons using metal hydrides. Not all hydrogen users requiring on-site hydrogen supply necessarily have access to a suitable waste gas stream however. It has also been proposed to separate hydrogen from dissociated ammonia by absorption/desorption on heated palladium. However the high costs associated

with the use of palladium-based separation has
generally led away from this technology.

The present invention is based on the dis-
covery that the use of metal hydride to separate
hydrogen from dissociated ammonia provides a cost
effective system for the supply of hydrogen to
intermediate-sized users of merchant hydrogen.

According to the present invention there is
provided a reactor system for the delivery of 28 to
2800 m³/day of hydrogen on site from a dissociated
ammonia feed stream by use of a bed of hydridable
material which exothermically and selectively absorbs
hydrogen from the feed stream and endothermically desorbs
hydrogen on demand characterised in that the system
comprises at least one flow through reactor having inner
and outer heat exchange shells with a bed of hydridable
material located coaxially therebetween, and means for
introducing in use, the feed stream to the hydride bed
and means for permitting the flow of waste gas or
hydrogen therefrom with means for providing uniform gas
flow with low pressure drop across the bed, and means
for circulating fluid through the heat exchanger shells
whereby heat may be extracted therefrom during absorption
of hydrogen from the feed stream and may be supplied
thereto when hydrogen is desorbed from the hydride bed.

It is an important feature of the invention
that the dimensions of the reactor system govern the
delivery rate of hydrogen from the system.   Thus the
system may be tailored exclusively to the needs of the
hydrogen user.   The performance of the reactor system
may be predicted semi-quantitatively by the equation

$$F = (D_1 + D_2)^2 L^2 \pi K \rho \, \Delta T / \Delta Ht$$

where

F = Hydrogen flow rate, moles/sec.

D_1 = Diameter of inner wall of the hydride
container, cm.

D_2 = Diameter of outer wall of the hydride container, cm.

L = Length of hydride bed, cm.

π = Constant = 3.14

5   K = Thermal conductivity of hydride bed, $cal.sec^{-1}.cm^{-1}.K^{-1}$

ρ = Density of hydride bed, g/cc

ΔT = Temperature difference between reactor wall and mid-point of the hydride bed, K

10   ΔH = Heat of adsorption of hydride, cal/mole

t = Charging or discharge time, sec.

and D_2 is related to D_1 by the relationship:

$$D_2 = D_1 + 8 \, [Kt \, \Delta T / \Delta H \rho W] \tag{2}$$

where   W = Moles of hydrogen per gram of hydride.

15 Rearrangement of Equation 2 gives

$$t\Delta T = 0.0156 \, (D_2 - D_1)^2 \, \Delta H \, \rho \, W/K \tag{3}$$

or if t is in hours

$$t\Delta T = 4.34 \times 10^{-6} \, (D_2 - D_1)^2 \, \Delta H \, \rho \, W/K \tag{4}$$

In a preferred system of the invention the
20 reactor system is capable of continuous delivery of
hydrogen by use of two or more flow-through reactors in
tandem operationally connected so that at any time at
least one of the reactors is capable of hydrogen delivery
by desorption from the hydride bed therein. By appropriate
25 connections one, or more, reactors may be used to absorb
hydrogen from the dissociated ammonia feed stream whilst
hydrogen is being desorbed from a further reactor.

The term "flow through reactor" as used
herein applies to one in which a waste stream having a
30 hydrogen concentration less than that of the inlet feed
stream is exhausted from the reactor during the charging
cycle thereby preventing a build up of non-hydrogen
components of the feed stream in the reactor system.

By use of a reactor system in accordance
35 with the present invention it is possible to reduce the

the cost of hydrogen to users in the intermediate
range by a factor of up to 2.

The heat transfer characteristics of the
flow-through reactor of the invention are at the heart
of its performance. The heat flow is interrelated to
flow rate, pressure and recovery. These variables
operate to establish the effective hydrogen absorption
pressure. This, in turn, determines the peak tempera-
ture within the pellet bed, which relative to the coolant
temperature establishes the temperature difference, ΔT,
causing heat flow. The flow-through reactor requires
no high pressure containment or components so that it
can be relatively large without being massive and has
a high surface-to-volume ratio to provide good heat
transfer. By applying hydrogen delivery requirements
to a relatively simple performance model based on heat
transfer considerations the necessary dimensions may
readily be deduced.

Cooordinated reactors can be designed to act
alternately so that while one unit is absorbing hydrogen,
the other is desorbing hydrogen. More than two units
can be used with appropriate timing. For example, if
the discharge time (DC) is 30 minutes and the charging
time (C) is 60minutes, then with 3 reactors cycled
as shown below, a continuous flow can be maintained with
one reactor delivering hydrogen while 2 are being
charged:

Time	Reactor 1	Reactor 2	Reactor 3
T + 0	DC		C
30	C	DC	
60			DC
90	DC	C	
120		DC	C
150	C		
180			DC

In this way hydrogen can be continuously provided. The
heat necessary for desorption can be provided in part
by the heat given off during the absorption phase and
by an external source. For example, hot water may be
used to provide required heat and cold water may be
circulated in the heat exchanger to aid in the absorption
phase.

The hydridable materials used in the reactor
system of the present invention are metals and alloys
which can react with hydrogen in a chemically reversible
manner to form hydride compounds. One class of hydri-
dable material is definable by the formula AB_x wherein
A is selected from the group of rare earth metals
(including yttrium) and calcium, substitutable in an
amount up to about 0.3 atom with a wide variety of
metals, B is selected from the group of nickel and cobalt
substitutable in an amount of up to about 1.5 atoms by
a wide variety of metals and x is a number between 3
and 8. Another class of hydridable materials comprises
pure or substantially pure elements from the group of
magnesium, titanium, vanadium and niobium. Another
class comprises AD_m alloys where A is one or more rare
earth metals including yttrium, D is one or both of
cobalt and nickel or a mixture thereof with one or more

of the elements Fe, Cu and Mn and m satisfies $1/3 \leq m < 3$. Still further examples of hydridable materials are RMg and RNiMg (where R = rare earth) series alloys disclosed in U.S. Patent No. 4,126,242, titanium-vanadium-iron alloys disclosed in U.S. Patent No. 4,111,689; titanium-manganese alloys as well as conventional Ti-Ni and Ti-Fe alloys disclosed in U.S. Patent No. 4,144,103 and conventional Zr-Ni, Mg-Ni and Mg-Cu alloys disclosed in U.S. Patent No. 4,110,425. Other alloy and inter-metallic compound systems involving two, three, four, five and even more elements are also known to form chemically reversible hydrides and are included within the ambit of the term hydridable material for purposes of the present specification and claims. The following are examples of suitable hydridable materials: $Fe_{0.8}Ni_{0.2}Ti$, $ZrCr_{0.5}Fe_{1.5}$, $LaNi_{4.7}Al_{0.3}$, MNi_4Al, (where M is mischmetal), $LaNi_4Cu$, and $La_{1-x}Ca_xNi_5$ (where $x \leq 0.5$).

In practice the hydridable material should have an ambient temperature pressure plateau of less than one atmosphere, not be subject to poisoning by ammonia at the levels of concentration of ammonia in the dissociation gas stream, and not be subject to nitride formation under the operating conditions of the reactor system.

In accordance with a preferred feature of the invention the hydrides are pelletised. This obviates problems arising from hydride expansion and contraction, and also from decrepitation during use which can give rise to a high pressure drop across the reactor beds. It also prevents the problems connected with the use of fine powders. Suitable pellets for use in the present process and a process for pelletization of hydridable materials have been disclosed in European Patent Application 56724A and the use of pellets in combination with ballast material has also been disclosed in European Patent 15106B. It has been found that

when used in the reactor system of the present
invention: 1) pelletization does not adversely reduce
the performance of the reactor during either the
hydriding or dehydriding phase; 2) the pellets are
stable under thermal cycling over the required tempera-
ture ranges; 3) pelletization does not reduce signifi-
cantly heat transfer in the hydride bed; 4) the pellet
and material can accommodate the volume changes of the
hydride and can contain the fine particles; and 5) the
pellets have a size and shape such that the pressure drop
in the flow-through reactor is very small. Pellets
may be used in conjunction with a ballast material.

The invention will now be described by
reference to the accompanying drawings in which:-

Figure 1 is a schematic of a flow through
reactor, shown in cross-section, for the production of
hydrogen from a dissociated ammonia stream.

Figure 2 is a graph of the relationship
between the temperature difference and the cycle time,
illustrating the effect - predicted by the reactor model
of the present invention - of decreasing the bed thickness
in order to decrease cycle time.

Figure 1 shows reactor 10 consisting of an
insulated cyclindrical housing 11 in which a cylindrical
container 12 packed with hydridable material 13 is
coaxially located between inner and outer heat exchanger
shells 14, 15. A support screen 16 for the pelletized
hydridable material 13 is located at the bottom of
cylindrical container 12, and the container 12 is also
provided with inlet conduit 17 and valve 18 for admitting
dissociated ammonia to hydride bed 13 and outlet conduit
19 and valve 20 for passage of effluent waste gas, or
for delivery of hydrogen during desorption. Inlet and
outlet conduits 21, 22 are for entry and exit of heat
exchange fluid into and out of outer shell 15 and inlet
and outlet conduits 23, 24 are for entry and exit of

heat exchange fluid to and from inner shell 14. Pressure gauge 25 measures pressure in the hydride bed 13 and relief valve 26 is to prevent over-pressurisation of bed 13. Pelletised hydridable
5   material is packed at a density of 1.1 to 5 g/cm³ to form the hydride bed 13.

In operation dissociated ammonia is admitted through conduit 17 into the container 12 whilst cooling fluid is circulated through the inner and outer heat
10   exchanger shells 14, 15. When hydrogen from the stream is fully absorbed on the hydride bed 13, as detected for example by assessing the hydrogen content of the effluent stream from the outlet 19, the stream of dissociated ammonia is switched to a second reactor (not shown)
15   and valve 18 closed. When hydrogen is to be desorbed from the hydride bed heated water may be circulated through the heat exchange shells 14, 15.

An example will now be described.

The hydridable material used in the example
20   is $LaNi_{4.7}Al_{0.3}$ which has a capacity of about 0.8 hydrogen/metal atom (H/M) at 137.9 kN/m² gauge. The absorption and desorption plateau pressures of 24.1 kN/m³ gauge and 413.7 kN/m² gauge at 90°C are attractive (in the laboratory and commercially) in relation to
25   hydrogen recovery efficiency and available thermal inputs. The alloy was pelleted with a silicone rubber binder (General Electric Ge 2567-012 clear) by the following procedure. The alloy was hydrided and dehydrided several times to produce - 325 mesh powder
30   and finally stabilised by slow exposure of the hydrided powder to air. The powder was milled with silicone rubber in ratio 95:5, pressed in a die at 207 MN/m² cured for 16 hours at 100°C and cut into pellets (0.635 cm cubes).
35   The reactor was constructed of 0.318 cm stainless steel cylinder walls fixed to flanged end

plates 1.27 cm thick.   The end plates were bolted to
1.25 cm thick manifold plates with O-ring seals.   Gas
was distributed through a chamber below the porous
support platform.   This platform was sealed to the
5   walls with silicone rubber to prevent channelling.   The
reactor was designed for pellets of lower density than the
pellets actually used.   As a result only about 30% of
the available heat transfer surface was in contact with
the pellet bed.   Therefore when comparing the experimen-
10   tal performance with the model, the actual bed length
was used rather than the length of the reactor.

The absorption and desorption tests were run
in an essentially isobaric manner at nominally constant
temperature of the cooling/heating water.   The operating
15   mode was selected to provide the most direct basis for
comparisons and extrapolation of performance trends rather
than those which would be most suited for ultimate use
of the apparatus.

The temperature and flow rate of the cooling/
20   heated water was controlled by an external bath circulator
and cooler.   Gas flow was measured using electronic
mass flow meters with 100 l/min. sensors.   In experiments
involving hydrogen separation from a mixed gas, electronic
flow meter sensors were used on both the inlet and outlet
25   gas streams.   The output from these sensors were coupled
to three readout units to indicate directly the 75%
H_2 + 25% H_2 inlet flow, the H_2 absorption flow, and the
N_2-enriched outlet flow.

The performance of the cylindrical flow-through
30   reactor for the separation of H_2 from dissociated ammonia
was evaluated in three parts.   The first was the
operation of the reactor in pure H_2 to provide base line
data for later comparisons.   The second part was the
operation in a 75% H_2 + 25% N_2 mixed gas made to simulate
35   dissociated ammonia.   The third part was the comparison
of the experimental results to the performance model

outlined above.

Pure Hydrogen Operation

A series of absorption and desorption tests were run with pure hydrogen. The experiments were carried out at a nominal temperature of 25°C. They showed the increasing rate of absorption and temperature excursion as the charging pressure is increased. The peak temperature at each pressure was quite close to that predicted by the Van't Hoff relation for the alloy. These test results are given in the Table and in Figure 2.

Hydrogen Separation

Hydrogen separation was evaluated using a 75% H_2 - 25% N_2 pre-mixed gas to simulate dissociated ammonia. Separations were performed using three different combinations of controlled operation parameters. Two tests were performed at a nominal temperature of 25°C and were structured to give slow and fast operation which correspond to high and medium H_2 recovery efficiencies. After these two tests, a pure H_2 adsorption was run to determine if there had been any adverse effect on the base line performance due to the mixed gas operation. This was followed by a third separation test run at a nominal temperature of 5°C. These test results are given in the Table and in Figure 2.

TABLE

Test No.	Test	T °C	t*, Hours	t*Δt	$\mid t\Delta T - t\Delta T\mid$	Deviation |%|
1	A	50	1.75	87.5	26.6	23.3
2	B	44	2.15	94.6	19.5	17.1
3	B	41	2.40	98.4	15.7	13.8
4	A	37	2.50	92.5	21.6	18.9
5	A	37	2.90	107.3	6.8	6.0
6	A	39	3.10	120.9	6.8	6.0
7	C	30	4.40	132.0	17.9	15.7
8	A	26	4.50	117.0	2.9	2.5
9	C	23	5.10	117.3	3.2	2.8
10	A	22	5.40	118.8	4.7	4.1
11	B	25	5.60	140.0	25.9	22.7
12	C	22	5.60	123.2	9.1	8.0
13	C	16	8.40	134.4	20.3	17.8
		Average		114.1		12.2

A = Absorption Tests - UHP-H_2
B = H_2 Separation Tests - 75% H_2 + 25% N_2
C = Desorption Tests - UHP-H_2
*t = Time for absorption or desorption to
       95% of capacity.

The separation test results show overall that good H_2 separation was achieved, and that it was in reasonable accord with the performance anticipated from the pure hydrogen base line data. Separation efficiencies for the tests fell between 65 and 70%.

Reactor Model

The performance model previously described predicts from Equation 4 that for a given system

$$t \Delta T = C \qquad (5)$$

where the constant, C, in Equation 5 is given by

$$C = 4.34 \times 10^{-6} (D_2 - D_1)^2 \Delta H \rho \ W/K \qquad (6)$$

when t is in hours.

From the data given in Table I and plotted in Figure 2 one finds a value for C of 114.1 hr·K with a maximum deviation of 23.3% and an average deviation of 12.2%. For the $LaNi_{4.7}Al_{0.3}$ alloy pellets used as the hydridable material in the prototype reactor ρ = 3.2 g/cm³, W = 0.0057 moles of hydrogen per g of hydride and ΔH = 7200 cal-mole. The reactor bed thickness, Δr, was 6.0 cm, thus $D_2 - D_1 = \Delta D = 2 \Delta r$ = 12 cm. Employing these values in Equation 6 gives a value for K of 7.19 x 10^{-4} cal.cm^{-1}.sec^{-1}.K^{-1}. The best independent determination of the thermal conductivity of the pellets gave a value for K of 8.2 x 10^{-4} cal.cm^{-1}.sec^{-1}.K^{-1}. There is thus good agreement between the behaviour of the flow-through reactor predicted by the performance model and the experimentally observed behaviour.

The general agreement between test data and the reactor model establishes the utility of the model for predicting effects of process or system variations.

For example, the original concept aim was that of a
system with a 1 hr cycle time for a 10°C temperature
difference.   Several variations of the reactor size
are shown in Figure 2, with reactor bed thickness, Δ r,
5   ranging from 6 cm to 2 cm.   Objectives may be accomplished
without change in any other dimension of the reactor.
This is possible because the void volume above the
pellet bed is about 3 times the volume of the bed itself.

Other alternatives are also possible.   For
10   example, if a hydride bed thickness of 2 cm presented any
problem, a value of 3 cm could be considered along with
certain other changes.   At 3 cm bed thickness, a 2.5 hr
cycle time would be required for a 10°C temperature
difference.   A 1 hr cycle time could be achieved if the
15   temperature differences was increased to 25°C.   This
could be done by increasing the system pressure or by
lowering the plateau temperature of the alloy by 15°C
(corresponding to a factor of about 2 decrease in the
isotherm pressure).

20   Another factor implicit in the model is
that the bed functions relatively uniformly over its
entire length.   If a breakthrough front becomes well
defined, then the model only applies in the region of
the front.   This could be accounted in the model, to a
25   first approximation, by modification of the time term
such that:

$$t \quad = \quad \frac{front\ length}{bed\ length} \quad x\ cycle\ time \qquad (7)$$

This effect could become significant as the bed length
30   increases.   The 15 cm bed length used in the demonstra-
tion test series showed only slight evidence of non-
uniform bed operation.   However, decreasing the bed
thickness to 3 or 2 cm, as in the above examples, would
increase the length to 30 or 45 cm.   At these lengths,
35   non-uniform bed operation is more likely and may require
introduction of Equation (7) into the model.   The effect

will be to increase the cycle time predicted by the
model.

Since the above considerations take into
account the thermal conductivity and density of the
5   pellets, system variations might be required for a
different pellet formulation.   It can be seen however
that considerable system flexibility exists which can
be predicted on the results of the demonstration reactor
and tailored to the needs of the user.   Following
10   the above tests the silicone bonded pellets were removed
from the reactor and were examined physically.   There
was no evidence of particulate formation, settling or
expansion, which changes could have lead with continued
cycling to packing and increasing back pressure within
15   the bed.   The pellets appeared to be unchanged from
their initial condition.

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Claims

1.   A reactor system for the delivery of 28 to 2800 m^3/day of hydrogen on site from a dissociated ammonia feed stream by use of a bed of hydridable material which exothermically and selectively absorbs hydrogen from the feed stream and endothermically desorbs hydrogen on demand characterised in that the system comprises at least one flow through reactor 10 having inner and outer heat exchange shells 14, 15 with a bed of hydridable material 13 located coaxially therebetween and means 17 for introducing, in use, the feed stream to the hydride bed 13 and means 19 for permitting the flow of waste gas or hydrogen therefrom with means for providing uniform gas flow with low pressure drop across the bed 13, and means 21, 22, 23, 24 for circulating fluid through the heat exchange shells 14, 15 whereby heat may be extracted therefrom during absorption of hydrogen from the feed stream and may be supplied thereto when hydrogen is desorbed from the hydride bed 13.

2.   A reactor system as claimed in claim 1 in which the system comprises two or more flow through reactors in tandem such that in use at least one reactor is in the desorption mode.

3.   A reactor system as claimed in claim 1 or claim 2 in which the hydridable material is pelletised in a porous plastic.

4.   A reactor system as claimed in claim 3 in which the hydridable material is used in combination with a ballast material.

5.   A reactor system as claimed in any preceding claim in which the hydridable material is one of the following alloys:- $Fe_{0.8}Ni_{0.2}Ti$, $ZrCr_{0.5}Fe_{1.5}$, $LaNi_{4.7}Al_{0.3}$, MNi_4Al (where M is mischmetal), $LaNi_4Cu$ and $La_{1-x}Ca_xNi_5$ (where $x \leq 0.5$).

6.   A reactor system as claimed in any preceding claim in which the reactor 10 comprises an insulated

cyclindrical housing 11 and the hydridable material 13 is disposed in a cylindrical container 12 located coaxially between inner 14 and outer 15 heat exchanger shells.

7.   A reactor system as claimed in claim 6 in which the hydrogen flow rate F can be predicted semi quantitatively by the following equation:-

$$F = (D_1 + D_2)^2 L^2 \pi K \rho \Delta T / \Delta Ht$$

where

F =   Hydrogen flow rate, moles/sec.

D_1 =   Diameter of inner wall of the hydride container 12, cm

D_2 =   Diameter of outer wall of the hydride container 12, cm

L =   Length of hydride bed 13, cm

π =   Constant = 3.14

K =   Thermal conductivity of hydride bed 13, $cal.sec^{-1}.cm^{-1}.K^{-1}$

ρ =   Density of hydride bed 13, g/cc

ΔT =   Temperature difference between reactor wall 11 and mid-point of the hydride bed 13, K

ΔH =   Heat of adsorption of hydride, cal/mole

t =   Charging or discharge time, sec.

and D_2 is related to D_1 by the relationship

$$D_2 = D_1 + 8 [Kt \Delta T / \Delta H \rho W]^{1/2}$$

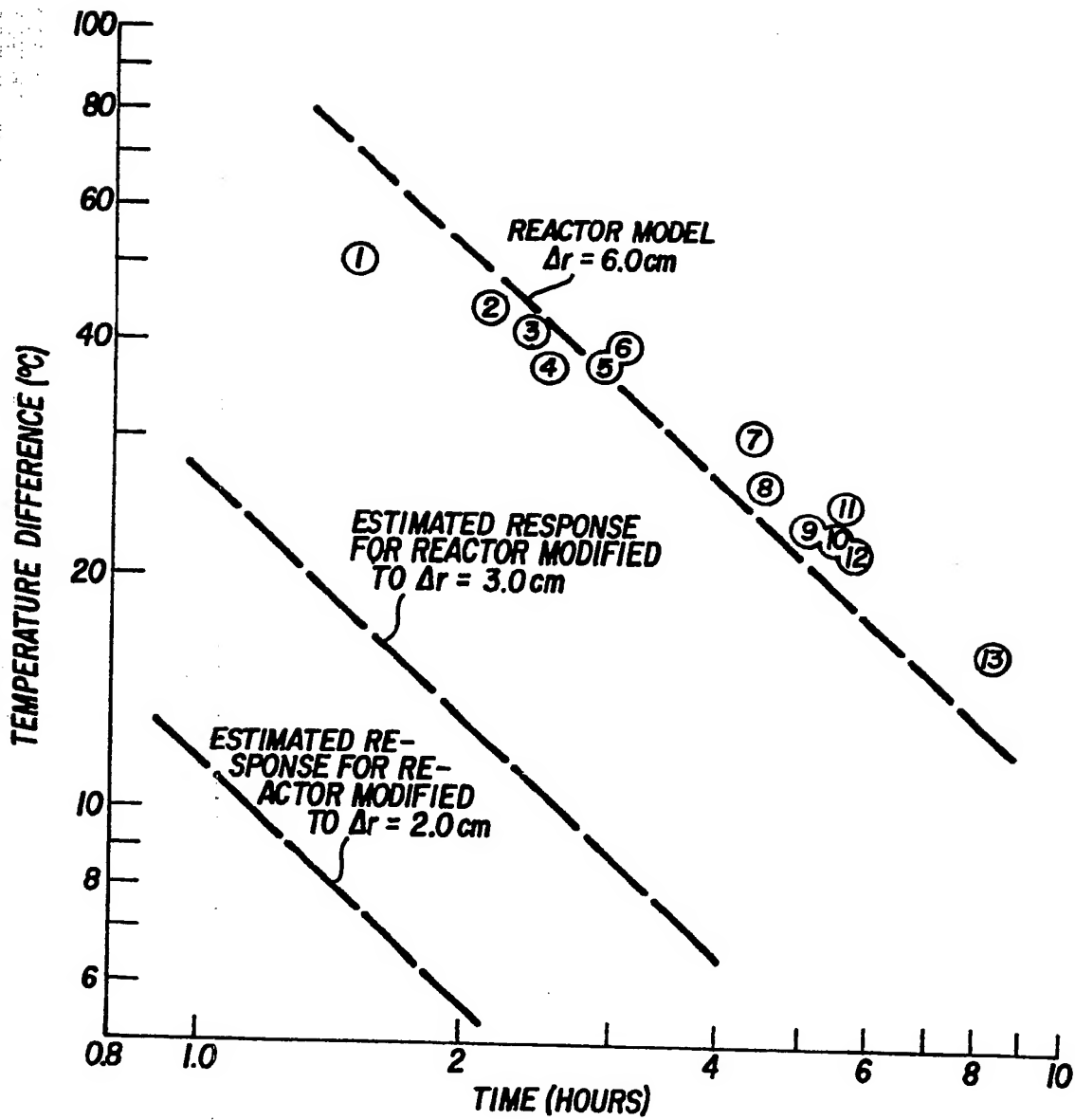where W = Moles of hydrogen per g of hydride.

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FIG. 1

FIG. 2